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Phase changes during solution casting of polymer blends containing cellulose

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SUMMARY

Morphological control of polymer solutions containing cellulose and synthetic polymers through spinodal decomposition was studied by optical microscopy inspection. The evolution of phase-separated structures depends highly on the ratio of the evaporation rate and the growth rate of concentration fluctuations. Regular bicontinuous structures result only when this ratio is sufficiently high. Then, the regular morphology develops at relatively high polymer concentration and is maintained as a whole in the course of evaporation.

INTRODUCTION

Polymer blends gain more and more importance both from a practical and academic point of view. Blends can be prepared via melt processing or solution casting. When cellulose is one of the blending components only the latter way is applicable for making of blends. The phase behavior of mixtures of cellulose and cellulose derivatives with synthetic polymers was studied to some extent [1-3]. Furthermore, it is known that cellulose turns out to be incompatible with synthetic polymers. Solution casting of incompatible polymers results generally in two-phase morphologies. However, this fact conveys the possibility to manipulate and to control the phase morphology in polymer blends [4,5]. It may be also interesting for designing of new fibers or membranes based on cellulose and synthetic polymers [6]. Thus, a largely open field is offered for studies of morphology and structure-property relationships. Morphologies similar to interpenetrating networks could be observed in blend fibers of cellulose with poly(acrylonitrile) (PAN) and poly(amide imide), respectively [7].

The mechanism and kinetics of thermally-induced phase separation in polymer blends have been the subject of extensive studies in recent years [8-12]. Similar mechanisms are operative when the phase separation in a solution of a polymer blend is induced by solvent evaporation. Structural evolution induced by solvent evaporation in ternary polymer solutions was analyzed as a function of evaporation rate, blend ratio and molecular weight [13]. Depending on the interactions bet-

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*To whom offprint requests should be sent ween the polymers and the rate of solvent evaporation the time evolution of concentration fluctuations leads to bicontinuous, periodic network-like phase-separated structures or to two-phase morphologies having irregular shape and size of domains. The periodic structures originate from phase separation via spinodal decomposition.

In this paper we present novel experimental results on structural evolution in solutions of highly incompatibel polymers. We address chiefly the question: Is it possible to observe in the course of phase separation periodic structures also in solutions of incompatible polymers? Systems used in this study were cellulose blended either with PAN or aramide. To elucidate the structure evolution the influence of evaporation history is investigated.

EXPERIMENTAL

The polymers used here are commercial products: Avicell-PH101® (cellulose) with an average degree of polymerization of 170, PAN with a weight-average molecular weight of 100,000 and the aramide fiber HW-50. The pair of dissimilar polymers was dissolved in the ratio 1/1 at 2 or 3 wt% of total polymer in lithium chloride (LiCl)/dimethyl acetamide (DMAc) as solvent. The LiCl-content in the solution amounted to 4 wt%. Prior to use the HW-50 fiber was extracted with hot DMAc for 10 min. The preparation of the polymer blend solutions is described in detail elsewhere [14]. All solutions studied here were clear and exhibited no insoluble polymer particles under a polarized optical micriscope (magnification: 500).

Film specimens of a thickness of about 0.1 mm were prepered by casting the polymer solution onto glass slides. After keeping them for 10 s or 15 min at room temperature the samples were heated rapidly and annealed at constant temperatures ranging from 60 up to 130°C until the phase-separated structures evolved completely. The evolution of structures was pursued using an optical microscope equipped with a heating stage. After evaporation of DMAc the samples contain still LiCl which makes them highly hygroscopic. Therefore, the samples must be stored carefully under sufficiently dry conditions.

RESULTS AND DISCUSSION

Structures as evolved from a solution of the four components Cell/PAN/LiCl/DMAc with the respective composition 1.5/1.5/4.1/92.9 in wt% are presented in Fig. 1. The structures of Fig.s 1a and 1b result after keeping the films for 10 s and 15 min, respectively, at room temperature followed by annealing at 60°C. Similar results are shown in Fig. 2 for the system Cell/HW50/LiCl/DMAc of the composition 1/1/4/94 in wt%. Fig.s 2a and 2b are the responses of the system when it is kept for 10 s at room temperature and afterwards annealed at

60 and 100°C, respectively. The structures depicted in Fig.s 2c and 2d, on the other hand, emanate when the samples were hold at room temperature for 15 min and afterwards annealed at 60 and 130°C, respectively.

The results shown in Fig.s 1 and 2 are in the first instant somewhat surprising. During the course of isothermal phase separation we observed the following: i) For samples kept for a very short period (10 s) at room temperature we found an evolution of periodic concentration fluctuations only at sufficiently high rates of evaporation. But the samples failed to form regular structures at slow evaporation. ii) With respect to the rate of evoporation the opposite is true for samples exposed for a more extended period (5 up to 15 min) to room temperature.

To understand the observed phenomena one has to recapitulate some basics on the mechanism of spinodal decomposition which governs the phase separation of polymer solutions in the unstable region. The growing rate R of concentation fluctuations is an increasing function of polymer concentration above the critical concentration. Obviously, with increasing concentration the mobility of the chain molecules declines leading also to a descent of the growth rate at higher polymer concentrations. Therefore, R displays a maximum as a function of polymer concentration.

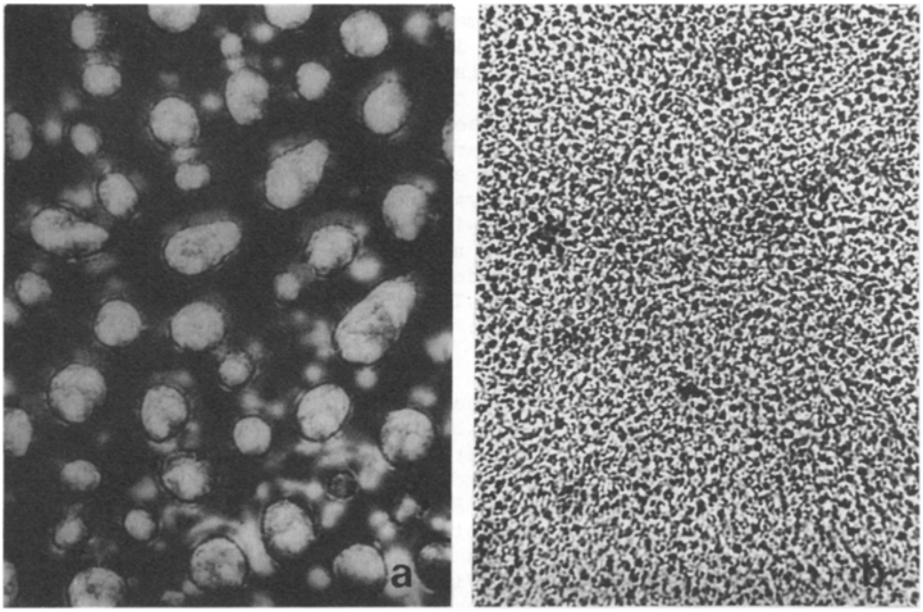

Figure 1: Light micrographs of decomposition structures evolved from Cell/PAN/LiCl/DMAc solution by keeping the cast films for 10 s (a) and 15 min (b) at room temperature followed by annealing at 60°C (⊢—⊣ 25 μm)

The wavelength of concentration fluctuations is a declining function of the polymer concentration. As a result, one has to compare two rate processes: the growth rate R of concentration fluctuations and the rate of evaporation R_E. According to CAHN's theory [15] the highest growth rate of concentration fluctuations is given by

$$R \sim \frac{D}{\Lambda_m^2} \qquad (1)$$

where D and Λ_m are an apparent diffusion coefficient and the wavelength of the concentration fluctuation having the highest rate of growth, respectively. The rate of evaporation is inversely proportional to a characteristic time τ. It follows that $\sqrt{D\tau}$ represents the distance X a chain molecule can diffuse within the period τ. Using Eq. (1) it follows

$$\frac{R_E}{R} \sim \frac{\Lambda_m^2}{D\tau} = \frac{\Lambda_m^2}{X^2} \qquad (2)$$

As a result one expects at

i) $R_E/R \ll 1$ - irregular phase morphologies,
ii) $R_E/R \approx 1$ - regular phase-separated structures.

When the rate of solvent evaporation is small phase separation will occur at low polymer concentration. Then, the mobility of the chain molecules is high and the regular concentration fluctuations (with a large wavelength) decay rapidly. Therefore, phase separation of the highly incompatible species will proceed to irregular phase-separated structures as shown in Fig.s 1a and 2a. On the other hand, in the case of a fairly high rate of evaporation appreciable phase separation is expected to occur at higher polymer concentration corresponding to concentration fluctuations with a smaller wavelength. Owing to the lower mobility of the molecules the regular structure formed at the critical concentration is maintained in the course of phase separation. This is demonstrated in Fig. 2b and analogeous results could be observed for solutions of cellulose and PAN.

The mobility is proportional to $\phi^{-\alpha}$ with $\alpha \geq 3$; ϕ is the polymer concentration. When the samples were kept for an extended period at room temperature slow evaporation occured which is leading to a reduced mobility. As a result the rate R is diminished or the ratio R_E/R is enhanced in comparision to the courses resulting in structures displayed in Fig.s 1a and 2a. Therefore, phase separation occurs at higher concentration corresponding, as before (cf. Fig. 2b), to a regular phase-separeted structure. This is shown in Fig.s 1b and 2c. At still higher rates of evaporation the phase separation starts at high polymer concentration which deviates much from the spinodal curve. In that case the thermodynamic driving force is high whereas the mobility is approximately the same as before

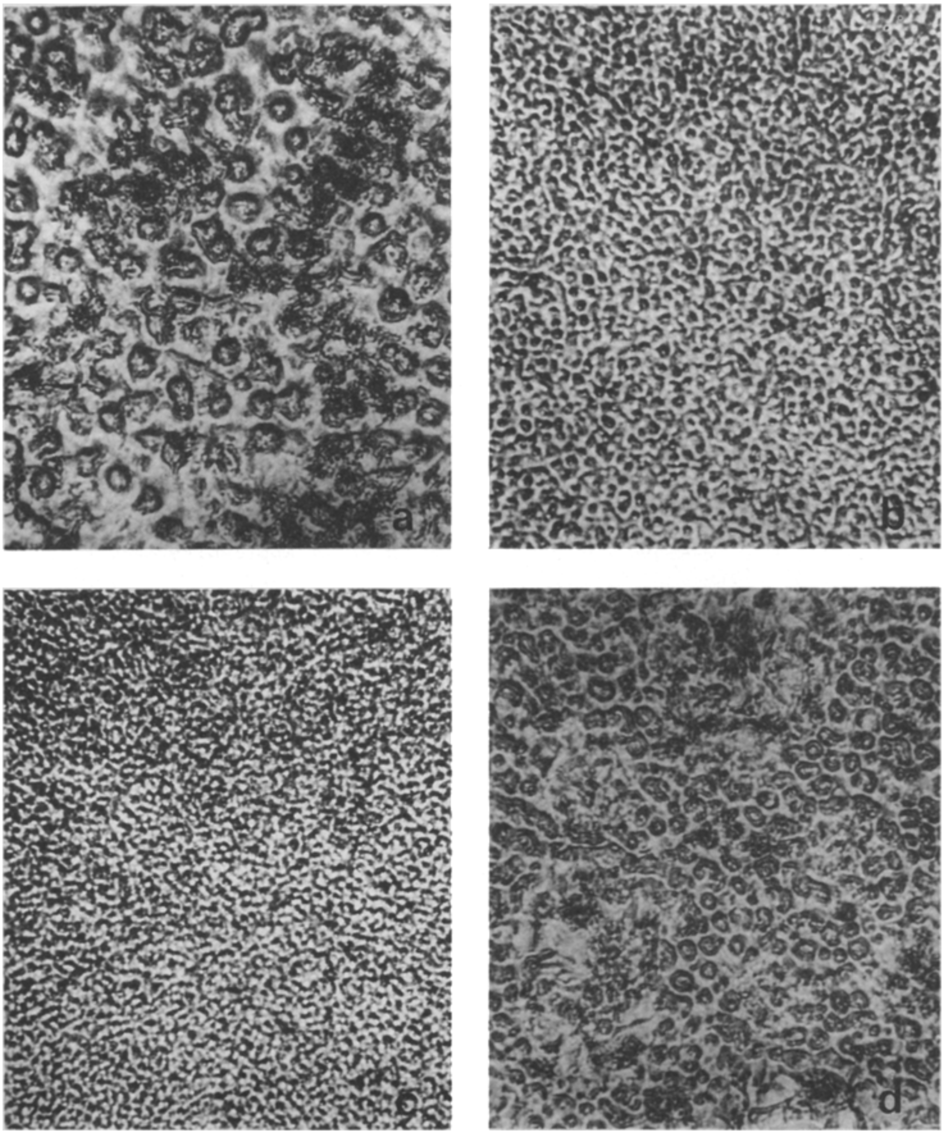

Figure 2: Light micrographs of decomposition structures evolved from Cell/HW50/LiCl/DMAc solution by keeping the cast films for a given time at room temperature followed by annealing at given temperature (a: 10 s / 60°C; b: 10 s / 100°C; c: 15 min / 60°C; d: 15 min / 130°C; ├──┤ 25 μm)

which actually means $R_E/R \ll 1$. Therefore, the system fails to form a regular structure but displays the macrophase-separeted morphology as shown in Fig. 2d.

In conclusion one may establish that the prevailing mechanism of phase separation leading to structure development by solvent evaporation in polymer solutions is the spinodal decomposition. The evolution of phase-separated structures depends highly on the ratio of the evaporation rate and the growth rate of concentration fluctuations. At sufficiently high values of this ratio regular phase-separated structures evolve whereas the systems studied here fail to form regular morphologies when the ratio is small.

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